



An improved back-flush-to-vent gas chromatographic method for determination of trace permanent gases and carbon dioxide in ultra-high purity ammonia



Maxim M. Trubyanov^{a,*}, Georgy M. Mochalov^a, Ilya V. Vorotyntsev^a,
Andrey V. Vorotyntsev^a, Sergey S. Suvorov^b, Konstantin Y. Smirnov^b,
Vladimir M. Vorotyntsev^a

^a Nanotechnology and Biotechnology Department, Nizhny Novgorod State Technical University n.a. R.E. Alekseev, 24 Minina str., 603950 Nizhny Novgorod, Russia

^b Firm HORST Ltd., 14-2-257 Akademika Yangelya str., 117534 Moscow, Russia

ARTICLE INFO

Article history:

Received 18 February 2016
Received in revised form 6 April 2016
Accepted 7 April 2016
Available online 8 April 2016

Keywords:

Ammonia
Trace impurities
GC-PDHID
Back-flush technique
Sodium hydrogen sulfate

ABSTRACT

A novel method for rapid, quantitative determination of trace permanent gases and carbon dioxide in ultra-high purity ammonia by dual-channel two-dimensional GC-PDHID is presented. An improved matrix back-flush-to-vent approach combining back-flush column switching technique with auxiliary NaHSO_4 ammonia trap is described. The NaHSO_4 trap prevents traces of ammonia from entering the analytical column and is shown not to affect the impurity content of the sample. The approach allows shortening the analysis time and increasing the amount of measurements without extensive maintenance of the GC-system. The performance of the configuration has been evaluated utilizing ammonia- and helium-based calibration standards. The method has been applied for the analysis of 99.9999% ammonia purified by high-pressure distillation at the production site.

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1. Introduction

Ultra-high purity (UHP) ammonia is used in electronic industry as the nitrogen source for the AlGaN/GaN epilayers in production of high brightness light-emitting diodes (LEDs), semiconductor lasers, and high electron mobility transistors (HEMTs). Purity control of ammonia is still a challenging problem stimulating continuous development of new instrumental and methodological approaches to trace analysis of impurities affecting optical and electrical performance of grown layers [1,2]. Gas chromatography has been proved to be the most versatile technique for purity control of hydride and corrosive gases and gained extensive application for measuring trace moisture, permanent gases, carbon dioxide, and light hydrocarbons in ultra-pure gases for electronic industry [3–17].

Nevertheless, ammonia is known to be a challenging compound for gas chromatography requiring special sample pre-treatment to avoid the deterioration of the GC-system. One of the useful solutions to address the problem is a complete removal of ammonia

from the sample [4]. The method allows rapid measurements of permanent gases at low-ppb levels using reactive $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ pre-column to remove ammonia from the sample with further GC-PID quantification of the impurities. The inconvenience is related to the loss of carbon dioxide reported with increasing number of ammonia injections. To overcome this problem an additional B_2O_3 reactant layer is proposed to be added to the pre-column taking into account that some amount of carbon dioxide which is initially retained in B_2O_3 has to be released by several injections of ammonia when setting up the blank value of CO_2 . Eventually the proposed approach serves to eliminate any contact of ammonia matrix with a GC system protecting it and reducing analysis time, but requires incorporation of purge and pre-treatment system for the reactive pre-column, and requires frequent replacement of the ammonia removal agents increasing total maintenance time. Besides that the method does not prevent such condensable impurities as CO_2 and H_2O from entering the molecular sieve column used for the separation of permanent gases which may cause degradation of the column separation efficiency in the long run.

An alternative method utilizing multiple switching columns can be applied to separate the impurity fraction from the matrix and then separate and detect the impurities [9–14]. However, due

* Corresponding author.

E-mail address: m.trubyanov@gmail.com (M.M. Trubyanov).

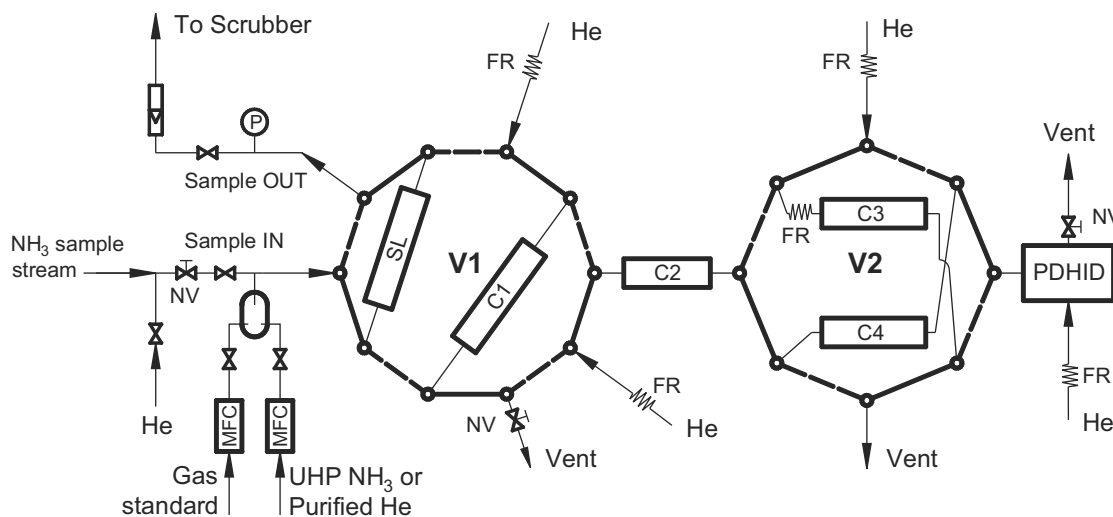


Fig. 1. A schematic diagram of the GC-PDHID back-flush-to-vent system for determination of trace permanent gases and carbon dioxide in ammonia: MFC—thermal mass-flow controller; P—pressure transducer; SL—sample loop; V1—10-port sampling and back-flush valve; V2—8-port column switching valve; C1—first column to separate the ammonia matrix from the impurities; C2—trace ammonia trap; C3, C4—analytical columns to separate the impurities; NV—needle valve; FR—calibrated flow restrictor; He—carrier gas; PDHID—pulsed discharge helium ionization detector.

to significant tailing of the ammonia peak an additional time-consuming temperature program is required to condition the first column for complete removal of ammonia otherwise it can generate constant background contamination and decrease the sensitivity of the detector.

This paper describes a novel approach to gas chromatographic determination of trace permanent gases and carbon dioxide in ammonia with a dual-channel two-dimensional GC-PDHID system employing back-flush column switching technique with an auxiliary NaHSO_4 trap to remove traces of ammonia. The configuration enables efficient removal of ammonia matrix by reversed flow of the carrier gas after the target impurities have been eluted from the first column. Two analytical columns are used for separation of permanent gases and carbon dioxide. The additional NaHSO_4 trap protects analytical columns and the detector from any traces of ammonia without affecting the impurity content of the sample. The performance data obtained for ammonia- and helium-based calibration standards is reported and discussed. The method has been applied to qualify the ammonia purified by high-pressure distillation in the production environment.

2. Experimental

A new two-channel system based on Chromos GC-1000 (Chromos Ltd, Russia) gas chromatograph equipped with a Valco PDHID system (D-2-I model, VICI, USA) has been developed to quantify trace H_2 , O_2 , N_2 , CH_4 , CO , and CO_2 in ammonia at low parts-per-billion levels ($1 \text{ ppb} = 10^{-9}\%_{\text{vol.}}$). The schematic diagram of the two-dimensional matrix back-flush-to-vent configuration along with the sampling manifold for the calibration and sampling is presented in Fig. 1. Detailed description of system components and optimized operating conditions are given in Table 1.

The GC system incorporates electrically actuated 10-port valve (V1) for sampling and back-flushing purposes and manual 8-port switching valve (V2) for column selection. Both valves are temperature-controlled and have helium purged housings. Research grade helium of 99.99999% purity (NII KM Ltd, Russia) used as a carrier and discharge gas was supplied from the cylinder with GCE electronic-grade stainless steel pressure regulator (GCE Group, Switzerland) utilizing Valco helium purifier (HP2 model, VICI, USA). Fixed in-line flow restrictors (FR) were used to achieve the required flow of the carrier gas and to equalize the resistances of

the switching lines minimizing the potential air leakage. Leak check procedure for all gas flow lines was carried out by purging each connection from the outside with a hydrogen flow and monitoring the background signal of PDHID. The signal of PDHID established for the running system without columns connected was not higher than 0.4 nA and after the columns were mounted and conditioned the signal was not higher than 0.7 nA .

The first column filled with 15%PEG-600/PTFE stationary phase (C1) is used to separate the impurity fraction from the ammonia matrix. 10-port sampling valve (V1) serves to introduce the sample into the column and back-flush the ammonia by reversing the flow direction of the carrier gas after the impurity fraction has been eluted but before the elution of the matrix. 8-port switching valve (V2) allows selection of the analytical column for impurity fraction separation keeping another column under the flow of helium. 13X molecular sieve column (C3) is used for separation of trace permanent gases, and Porapak Q column (C4) is selected for carbon dioxide. The columns were obtained from Chromos Ltd. and Tswet JSC, Russia. To minimize PDHID baseline fluctuations related to valve change operation the flow-rates of switching lines were accurately balanced by calibrated flow restrictors (FR) and by adjusting the needle valves (NV) placed on the vent line. Trace ammonia trap (C2) filled with NaHSO_4 (Ekros-Analitika Ltd., Russia) is mounted before the analytical column to remove any traces of ammonia that may come from the first column (C1) protecting the analytical column and the detector.

Ammonia- and helium-based mixtures of impurities at sub-ppm levels were generated by mass-flow mixing of the helium-based reference mixture with the flow of diluent gas, which is either 99.99999% ammonia (AirProducts, USA) or 99.99999% helium obtained from Valco helium purifier, in accordance with the ISO 6145-7 standard [18]. The schematic diagram of the calibration manifold is shown in Fig. 1. Two helium-based reference mixtures containing near 5 ppm and near 15 ppm of each component (15% tolerance) with the expanded uncertainty of 3% of the concentration were certified reference materials produced by Monitoring Ltd., (Russia) according to Technical Requirements number 6-16-2956 “Calibration gas mixtures. Technical standard conditions” under control of D.I. Mendeleyev Institute for Metrology (VNIIM), Moscow, Russia. The thermal mass-flow controllers with an accuracy of 1% at full scale (15 ml/min, 60 ml/min, and 150 ml/min) were purchased from Eltchpribor Ltd., Zelenograd, Moscow region,

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